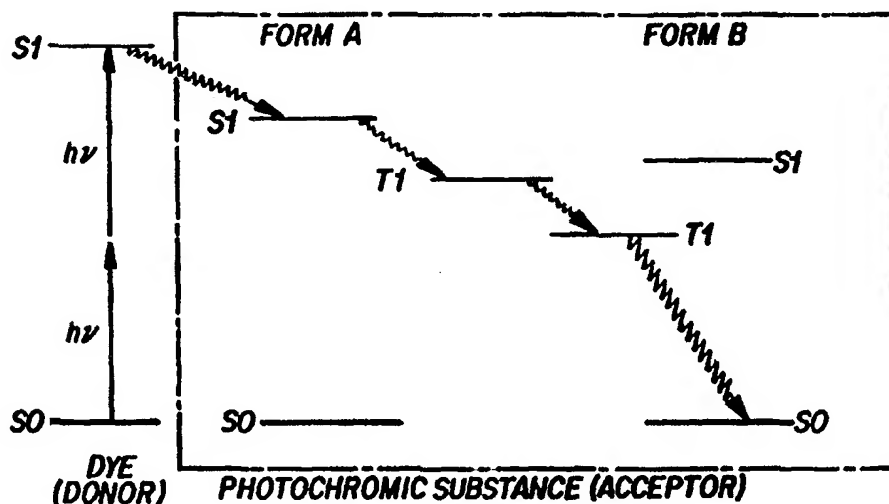




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>G03C 1/73, G11B 7/24</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 00/05624</b> <b>(43) International Publication Date:</b> 3 February 2000 (03.02.00)
<b>(21) International Application Number:</b> PCT/US99/16419 <b>(22) International Filing Date:</b> 21 July 1999 (21.07.99) <b>(30) Priority Data:</b> 60/093,508      21 July 1998 (21.07.98)      US <b>(71) Applicant (for all designated States except US):</b> TRID STORE IP, L.L.C. [US/US]; Dr. Alexander Libin, 4th Floor, 747 Third Avenue, New York, NY 10017-2803 (US). <b>(71) Applicant (for US only):</b> KOROTEEV, Nina (executrix for the deceased inventor) [RU/RU]; Vorob'evy Gory, MGU, Bld. M., Suite 166, Moscow, 117296 (RU). <b>(72) Inventor:</b> KOROTEEV, Nikolai I. (deceased). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> LEVICH, Eugene, V. [IL/US]; Apartment 9L, 330 West 45 Street, New York, NY 10036 (US). MAGNITSKII, S. A. [RU/RU]; Flat 76, 9 Garibaldi Street, Moscow, 117313 (RU). MALAKHOV, D. V. [RU/RU]; Flat 339, 51/2 Kashirskoye Shosse, Moscow, 115612 (RU). SHUBIN, V. V. [RU/RU]; Ap. 143, Michurinsky Pr. 54 block 3, Moscow, 117192 (RU).		<b>URSNOYOV, Zh. S. [RU/RU];</b> Vorobjevy Gory V-466, Moscow, 117234 (RU). <b>(74) Agents:</b> COHEN, Herbert et al.; Blank Rome Comisky & McCauley LLP, Suite 1000, 900 17th Street, N.W., Washington, DC 20006 (US). <b>(81) Designated States:</b> AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>

**(54) Title:** INCREASING WRITING EFFICIENCY IN 3D OPTICAL DATA STORAGE SYSTEM

**(57) Abstract**

As shown in the figure, a dye donor interacts with the incident laser radiation ( $h\nu$ ), is excited from a ground state  $S_0$  to an excited state  $S_1$ , and transfers this to form A of a photochromic dye which converts to form B and undergoes a decay to the ground state. The dye donor may be either a fluorescent dye or a dye which is a non-linear optical material, such as a second harmonic generation material. The donor and photochromic materials may be in separate layers or may be mixed together in a single layer. A subpicosecond semiconductor laser or an femtosecond argon ion pumped Ti:Sapphire laser can be used as laser source. The interaction of the dye with the laser radiation may be a two photon interaction.

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakistan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

## INCREASING WRITING EFFICIENCY IN 3D OPTICAL DATA STORAGE SYSTEM

### BACKGROUND OF THE INVENTION

#### 1. Field of the Invention.

- 5 1. The present invention generally concerns to 3D optical memory system development and memory media investigations. This invention is related with using a nonlinear properties (optical H-G and TPA) of thin polymeric films in 3D optical data storage systems.

#### 2. Background of the invention.

- 10 The need for enhancement of the capacity of computer data storage systems has been increasing in the past decade. The modern optical and magneto-optical systems will exhaust their resource soon. Thus the necessity of creating new more capacitive memory systems such as 3D optical memory devices has appeared.

- 15 The 3D optical memory principle have a physical limit of information capacity -  $1\text{Tbit/cm}^3$ . This resource can be used only if the direct access to the information pit inside the volume is realized. The informative media can be made of a photochromic compound embedded into a polymer matrix. The photochromic material under light illumination transforms into the stable photoinduced form, which can be registered by phase or amplitude read-out method.

- 20 The localization of writing, and reading information in 3D optical data storage system can be achieved only by non-linear processes, for example by TPA or by HG. The 3D optical memory systems based on TPA or HG processes are very promising because of possibility to write, read and erase information inside the local volume of photochromic media. It is well known that the TPA cross sections of the most of organic photochromic materials are in the range  $1\text{--}10\text{ GM}$  ( $1\text{ GM}=1\cdot 10^{-50}\text{ cm}^4\text{s}$ ). As a source of radiation in 3D erasable optical memory system based on two photon induced photoreaction one now needs a powerful laser system like Nd:YAG or Ti:sapphire. The current values of TPA cross section are not enough for writing information with the help of compact semiconductor lasers. Thus the problem of increasing effective TPA cross section is of a
- 30 crucial importance.

## OBJECT AND SUMMARY OF THE INVENTION

Two methods of increasing efficiency of writing information in 3D optical memory devices are proposed.

Two-stage method

5           The first (two-stage) method consists in a passing of two photon absorption of photochromic material to frequency conversion (optical harmonic generation) in an additives with high non-linearity.

10           Let us consider the SHG as an example of optical harmonic generation with high frequency conversion efficiency. In this method a process of recording is divided into two stages. In the first stage the SHG of laser radiation in the thin organic film occurs. The SH frequency coincides with maximum of absorption band of photochromic material initial form. On the second stage the SH radiation induces photoreaction in a photochromic material by single-photon absorption. The informative medium consists of the sequence of such layers (FIG. 1). To prevent an undesirable illumination of other  
15           layers by SH radiation one can use additional layers absorbing SH radiation completely. In principle, when one uses highly absorbing photochromic material it is not necessary to use any additional absorbing layers. In generally, nonlinear optical and photochromic layers can be combined in one. The efficiency of writing process can be substantially increased if one can achieve a maximum efficiency of SHG process and use a  
20           photochromic material with the high value of single-photon absorption cross section and high quantum yield of photoreaction.

Two-stage method application for ROM disks

25           The reading of information can be realized by registration of fluorescent signal from informative cell (pit) under its illumination by radiation with wavelength within absorption band of fluorescent media.

30           One of the serious problems, limiting the capacity of 3D optical memory disks in readout process under linear excitation of fluorescence, is a high density of writing information in neighboring layers. In this case the informative disk actually presents a homogeneous media with photoactive substance in 'written' form. Thereby the informative disk becomes practically opaque for the readout light, go there are practically no access to the deeply lying informative layers. Proposed two-stage. method of making a

nonlinear-optical disk allows to solve this problem. The reading process is based on TPA process.

In the layer with nonlinear material the SHG occurs. Then the SH radiation excites the fluorescence of photochromic material in written area.

5 Using this two-stage method one can make the multilayer informative fluorescent disk (FIG. 1).

The energy transfer method

10 The second (energy transfer) method is based on using a mechanism of energy transfer from high TPA dyes, to the photochromic molecules. The TPA cross sections of some organic dyes and chromophore molecules can be equal to 100-10000 GM. Recently a new chromophore with TPA cross section equals to 19400 GM was synthesized. Due to energy transfer mechanism it is quite reasonable to use these substances as a sensitizer of photoisomerization reaction. Such an approach has the advantages that the energy transfer process in organic compounds is deeply investigated. The efficient energy transfer is  
15 possible if the fluorescence spectra of the energy donor molecule is overlapped with the absorption spectra of the acceptor molecule.

DESCRIPTION OF THE DRAWINGS

FIG. 1. Principle scheme of two-stage method.

FIG. 2. Absorption spectra of (II A) and (II B) in PMMA film.

20 FIG. 3. Experimental scheme for measurement of writing efficiency. The 1- is electrooptical modulator, 2- are light filters, 3- is monochromator, 4-is CCD camera, 5- is read record head, 6-is sample, 7-is 3D positioning device, 8-is objective (N.A.=0.20, x10), 9-is halogen lamp.

FIG. 4. Accumulation kinetics of photoinduced form (II) (squares) and TCM (triangle)  
25 under light excitation (irradiation time is 1-10 ms).

FIG. 5. The scheme of the, energy transfer principle from the high TPA dye (donor) to the photochromic material (acceptor).

FIG. 6. Absorption spectra of (II)(dashed line), (IV) (dotted line) and fluorescence spectra of (IV) (solid line) in arbitrary units.

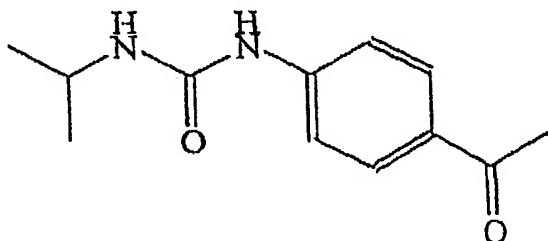
30 FIG. 7. The main requirements to the photochromic system with the energy transfer.

## DESCRIPTION OF THE INVENTION

Two-stage method

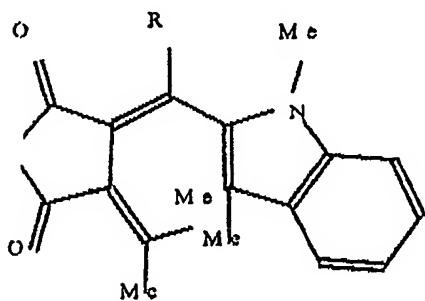
The FIG. 1 shows the scheme of two component informative media (TCM) for two-stage method of writing information.

This TCM consists of two layers. In the first layer the SHG of laser radiation in thin nonlinear organic film occurs. For example, thin nonlinear organic film can be made of polycrystal isopropyl-4-acetylphenylurea (I), as a source of laser radiation the femtosecond Ti:sapphire laser (wavelength 810 nm) can be used.

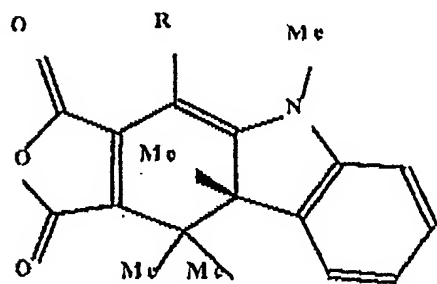


(I)

The SH frequency (wavelength 405 nm) coincides with maximum of absorption band of photochromic material initial form. For example, a photochromic material can be idoly fulgide (II) embedded into polymethylmethacrylate (PMMA) film, We will refer to (II B) as the photoinduced form of (II). The initial form of (II) is (II A).



(II A)



(II B)

The absorption spectra of (II A) and (II B) are shown in FIG. 2.

Then the SH radiation is absorbed by photochromic material (II A) and a photochemical reaction is induced, i.e. (II A) transforms into (II B). To prevent an undesirable illumination of other layers by SH radiation one can use additional layers  
 5 absorbing SH radiation completely. If possible the nonlinear-optical material and a photochromic substance can be combined in one layer.

It is important that the fundamental radiation of Ti:sapphire laser is not absorbed in any layer except the layer, where the process of writing occurs. This allows to use many layers without crosstalks between them.

10 The efficiency of writing was measured with the help of specialized setup. The scheme of this setup is depicted in FIG. 3. The Ti:sapphire laser beam is used as a source of radiation for inducing the photoreaction. The laser beam is modulated with the help of the electrooptical modulator. The induced optical density is measured after illuminating the sample by different doses of irradiation. As a probe beam the monochromatic light  
 15 (wavelength 540 nm) of halogen lamp is used.

The writing, efficiency is defined by the efficiency of TPA process (the value of effective TPA cross section\*).

The rate of photochemical reaction can be expressed in the following way:

$$\frac{\partial N}{\partial t} = -\sigma \phi_2 N \quad \text{for linear absorption,}$$

$$20 \quad \frac{\partial N}{\partial t} = -\delta \phi_1^2 N \quad \text{for TPA,}$$

where N - is the concentration of (II B),  $\phi_1$  and  $\phi_2$  - are the photon fluxes density of fundamental and double frequency of radiation respectively,  $\sigma$  - is the linear absorption cross section,  $\delta$  - is the effective TPA cross section.

$$\text{For effective TPA cross section we have: } \delta = \frac{64\pi^5 h \sigma \chi_{eff}^2 L^2}{n_1^2 n_2 \lambda_1^3},$$

25 where  $\chi_{eff}$  is a quadratic nonlinearity, L - is the media length,  $n_1$ ,  $n_2$  - are media

---

\* effective TPA cross section is the measured TPA cross section of the media

refractive indexes at fundamental and double frequency radiation respectively,  $\lambda_1$  - is fundamental wavelength.

However the efficiency of writing can be calculated from the experimental results using the following expressions

$$\delta = \frac{bf\tau S^2 (\hbar\omega)^2}{gW^2}$$

where  $W$  - is an average power of radiation,  $S$  - is the light spot square,  $f$  - is a pulse repetition rate,  $g$  - is a form factor of laser pulse,  $\tau$  - is the laser pulse duration,  $w$  is the frequency of fundamental radiation,  $b$  - is a slope of accumulation of photoinduced form (II B) concentration as a function of irradiation time at the initial part of the curve.

The FIG. 4 shows the dependencies of the photoinduced form concentrations on the irradiation time. Curve 1 and 2 correspond to the (II) in PMMA and TCM system respectively. From the comparison of these two curves one can see the strong increase of writing efficiency in the TCM. For example a TCM consisting of I and II shows the 32 times increasing of writing efficiency.

#### Two-stage method application for ROM disks

One of the serious problems limiting the capacity of 3D optical memory disks in readout process under linear excitation of fluorescence is a high density of writing information in neighboring layers. In this case the informative disk actually presents a homogeneous media with photoactive substance in 'written' form. Thereby the informative disk becomes practically opaque for the readout light, so the access to the deeply lying informative layers becomes practically impossible. Proposed two-stage method of making a nonlinear-optical disk allows to solve this problem. The reading is based on TPA process.

In the layer with nonlinear material the SHG occurs. Then the SH radiation excites the fluorescence of photochromic material in written area. In given scheme nonlinear layers can be much thicker then photoactive layers. Such structure allows to provide high writing density (submicron pit size) and to increase the effective TPA cross section simultaneously. For example the nonlinear layers can be made of nonlinear MNA (m-nitroaniline crystals (III)). This organic crystal is transparent wavelengths larger than 0.5 $\mu$ m, so it can not be used for erasable optical disks containing photochromic material,



whose absorption band is near 0.4 $\mu$ m. However, it is possible to use this crystal in ROM disks for realization of reading process. For example if the thickness of nonlinear layers is equal to 100  $\mu$ m, the effective TPA cross section will be more than  $10^5$  GM. As a source of radiation, a compact subpicosecond semiconductor laser can be used. From the principle of disk structure it is clear that there is practically no limit for layer number except only the geometric considerations.

#### The energy transfer method

The FIG. 5 shows the principle scheme of energy transfer method of increasing of the writing efficiency. One can expect a significant enhancement of writing efficiency if the energy transfer from high TPA dye to a photochromic molecule takes place.

The rate of photochemical reaction (A-B) with energy transfer is:

$$\frac{dn_B}{dt} = -n_B(\varphi_{BA}\delta_B + \varphi_{BA}\delta_A)\phi^2 + n_0\varphi_{AB}\delta_A\phi^2 + n_D(\varphi_{AB}\varphi_{trA} - \varphi_{BA}\varphi_{trB})\delta_D\phi^2,$$

where  $n_B$  - is a photoinduced form concentration (B),  $n_0$  - is a total concentration of photochromic substance (A+B), ( $\varphi_{AB}$  and  $\varphi_{BA}$  - are quantum yields of direct (A-B) and reverse (B-A) photoreactions,  $\delta_A, \delta_B$  and  $\delta_D$  - are TPA cross sections of form A, B and donor molecules respectively,  $\varphi_{trA}$  and  $\varphi_{trB}$  - are efficiencies of energy transfer to form A and B respectively,  $\Phi$  - is a pulse photon density.

In the case of small concentration changes one can integrate this equation and receive the following expression:

$$b = (n_0\varphi_{AB}\delta_A + n_D(\varphi_{AB}\varphi_{trA} - \varphi_{BA}\varphi_{trB})\delta_D - n_B^0(\varphi_{BA}\delta_B + \varphi_{AB}\delta_A))\frac{gE^2}{\tau},$$

where  $b$  - is the slope of form (B) concentration dependence on number of pulses ( $k$ ) at the initial part of the curve,  $E$  - is a pulse energy,  $g$  - is a laser pulse form factor and  $\tau$  - laser pulse duration. The effectiveness of energy transfer can be calculated from the following expressions:

$$\varphi_{trA} = \frac{K_{D-A}}{\frac{1}{\tau_d} + K_{D-A}}$$

$$K_{D-A} = \frac{1}{\tau_d} \left( \frac{R_0}{R} \right)^6;$$

$$R_0^6 = \frac{9000 \ln 10 \kappa^2 \varphi_d}{128 \pi^5 n^4 N_A} \int \frac{F_p(\nu) \varepsilon_A(\nu)}{\nu^4} d\nu$$

where R - is a distance between molecules of donor and acceptor,  $K_{D-A}$  - is the  
 5 constant of the energy transfer rate between donor and acceptor under assumption of  
 dipole-dipole interaction,  $R_0$  - is a Ferster radius,  $\tau_d$  - is the excited state of donor  
 molecule lifetime (without acceptor molecules),  $\kappa$  - is an anisotropy factor (for free-  
 oriented molecules  $\kappa^2=2/3$ ), ( $\varphi_d$  - is a quantum yield of donor fluorescence, n - is the  
 index of media refraction,  $N_A$  - is an Avogadro constant,  $F_p(\nu)$  - is the molecular  
 10 fluorescence spectrum (the dependence of the absolute number of emitted photons on the  
 wavenumber  $\nu$ ) normalized to  $1(\int F_p(\nu) d\nu = 1)$ ,  $\varepsilon_A(\nu)$  - is the molar extinction  
 coefficient.

The efficiency of the energy transfer is defined by Ferster radius  $R_0$ , lifetime of the  
 excited state  $\tau_d$  and concentration of the acceptor molecules.

15 The significant increasing of two-photon photoisomerization efficiency can be  
 achieved by using a high TPA cross-section dye-sensitizer. The value of  $R_0$  is defined by  
 mutual overlapping between the fluorescence spectrum of donor and absorption spectrum  
 of acceptor. The higher overlapping of spectra leads to the higher efficiency of energy  
 transfer (if  $K_{DA} \ll 1/\tau_d$ ). The value R is defined by the donor and the acceptor molecule  
 20 concentrations.

Thus the right choice of photochromic substance - dye system should be made in  
 accordance with many parameters. The main criteria of this choice are shown in FIG. 7.

For example, as a dye we use a Rhodamine 6G (IV) and (II) is used as a  
 photochromic material. The energy transfer system was made as a mixture of (II) and (IV)

in PMMA film. The absorption spectra of this system components are depicted in FIG. 6, One can see that the absorption band of photoinduced form of (II B) is overlapped with fluorescence band of (IV) and the effective energy transfer is possible from (IV) to the photoinduced form (II B). The photoinduced form was preliminary accumulated by illumination of the sample with the monochromatic light (400 nm) and then was tested by the same method as TCM system. The effectiveness of the energy transfer and effective cross sections are shown in table 1.

TABLE 1.

	TPA cross section, GM	Efficiency of energy transfer, $\phi_{tr}$
II	$0.05 \pm 0.02^*$	
IV	$200 \pm 70$	
II + IV	$2.7 \pm 0.8^{**}$	$0.04 \pm 0.02$

\* - effective cross section,

\*\* effective cross section for reaction (II B)->(II A).

What is claimed is:

1. An optical recording medium for 3D optical data storage devices comprises at least one recording layer containing a composition which includes:

at least one dye and

at least one photochromic compound,

the improvement that

said dye is a fluorescent, possessing high-TPA cross section for exciting illumination dye and is a donor of electronic energy transfer to the acceptor,

said photochromic compound has a high photochemical reversibility, thermal stability and an absorption spectrum which is overlapped with the fluorescence spectrum of said dye, and

a concentration of said photochromic compound is in excess comparatively to concentration actually required for energy transfer from said dye to said photochromic compound.

2. A method for recording (erasing) information on an optical recording medium comprising at least one recording layer containing a composition which includes:

at least one dye and

at least one photochromic compound,

the improvement that

said dye is a fluorescent, possessing high-TPA cross section for exciting illumination dye and is a donor of electronic energy transfer to the acceptor,

said photochromic compound has a high photochemical reversibility, thermal stability and an absorption spectrum, which is overlapped with the fluorescence spectrum of said dye, and

a concentration of said photochromic, compound is in excess comparatively to concentration actually required for energy transfer from said dye to said photochromic compound,

which method comprises:

a mixing of said photochromic compound and said dye, and thereby converting a part of electronic energy from said dye to said

photochromic compound leading to photoisomerization reaction of said photochromic compound,  
a covalent bonding of said photochromic compound and said dye, and  
thereby  
converting a part of electronic energy from said dye to said photochromic compound leading to photoisomerization reaction of said photochromic compound.

3. A method for increasing recording efficiency on an optical recording medium comprising at least one recording layer containing a composition which includes:

at least one dye and  
at least one photochromic compound,  
the improvement that  
said dye is a fluorescent, possessing high-TPA cross section for exciting illumination dye and is a donor of electronic energy transfer to the acceptor,  
said photochromic compound has a high photochemical reversibility, thermal stability and an absorption spectrum, which is overlapped with the fluorescence spectrum of said dye, and  
a concentration of said photochromic compound is in excess comparatively to concentration actually required for energy transfer from said dye to said photochromic compound,  
which method comprises:  
a mixing of said photochromic compound and said dye, and thereby  
converting a part of electronic energy from said dye to said photochromic compound leading to photoisomerization reaction of said photochromic compound,  
a covalent bonding of said photochromic compound and said dye, and  
thereby  
converting a part of electronic energy from said dye to said photochromic compound leading to photoisomerization reaction of said photochromic compound, and  
the significant increasing of recording (erasing) efficiency.

4. An optical recording medium for 3D optical data storage devices comprises at least one recording layer containing a composition which includes:

at least one nonlinear compound and

at least one photochromic compound,

the improvement that

said nonlinear compound possesses a high quadratic (cubic) nonlinearity,

a high laser threshold damage, transparency at recording (erasing),

reading wavelengths, a thermal and time stability,

said photochromic compound has a high photochemical reversibility, thermal

stability and has an absorption spectrum, which wavelength maximum

coincides with the wavelength of frequency converted illumination,

a thickness of said nonlinear compound and the value of nonlinearity of said

nonlinear compound is in excess for the efficient frequency conversion.

5. A method for recording (erasing) information on an optical recording medium comprising at least one recording layer containing a composition which includes:

at least one nonlinear compound and

at least one photochromic compound,

the improvement that

said nonlinear compound possesses a high quadratic (cubic) nonlinearity,

a high laser threshold damage, transparency at recording (erasing),

reading wavelengths a thermal and time stability,

said photochromic compound has a high photochemical reversibility, thermal

stability and has an absorption spectrum, which wavelength maximum

coincides with the wavelength of frequency converted illumination,

a thickness of said nonlinear compound and the value of nonlinearity of said

nonlinear compound is in excess for the efficient frequency conversion,

which method comprises:

a preparation of said photochromic compound and said nonlinear

compound, and thereby

converting of frequency by optical harmonic generation in said

nonlinear compound,

absorption of frequency converted illumination by said photochromic

compound leading to photoisomerization reaction of said photochromic compound.

6. A method for increasing recording efficiency on an optical recording medium comprising at least one recording layer containing a composition which includes:

at least one nonlinear compound and

at least one photochromic compound,

the improvement that

said nonlinear compound possesses a high quadratic (cubic) nonlinearity,

a high laser threshold damage, transparency at recording (erasing),

reading wavelengths, a thermal and time stability,

said photochromic compound has a high photochemical reversibility, thermal

stability and has an absorption spectrum, which wavelength maximum

coincides with the wavelength of frequency converted illumination,

a thickness of said nonlinear compound and the value of nonlinearity of said

nonlinear compound is in excess for the efficient frequency conversion,

which method comprises:

a preparation of said photochromic compound and said nonlinear compound, and thereby

converting of frequency by optical harmonic generation in said nonlinear compound,

absorption of frequency converted illumination by said photochromic compound leading to photoisomerization reaction of said photochromic compound, and thereby

the significant, increasing of recording (erasing) efficiency.

7. A method for reading information in 3D ROM system from an optical medium comprising at least one informative layer containing a composition which includes:

at least one nonlinear compound and

at least one photochromic compound,

the improvement that

said nonlinear compound possesses a high quadratic (cubic) nonlinearity,

a high laser threshold damage, transparency at recording (erasing),

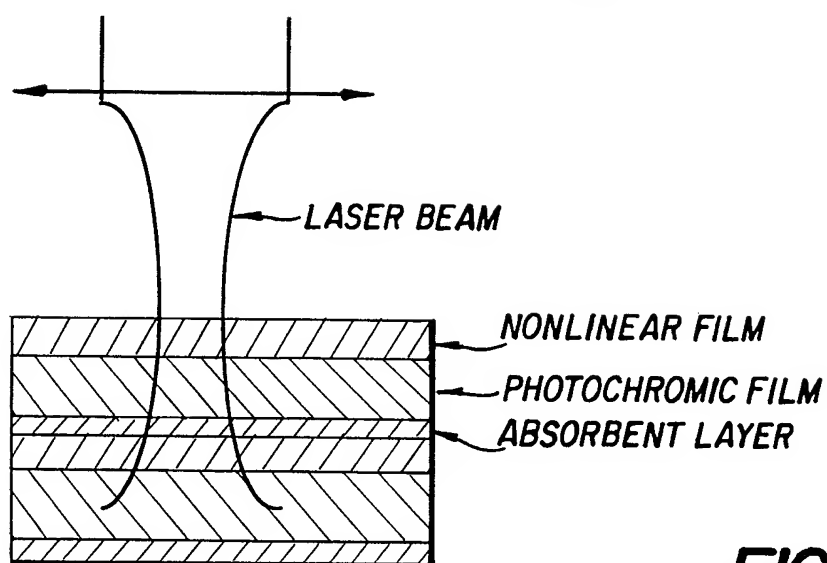
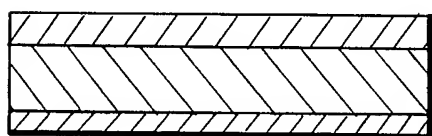
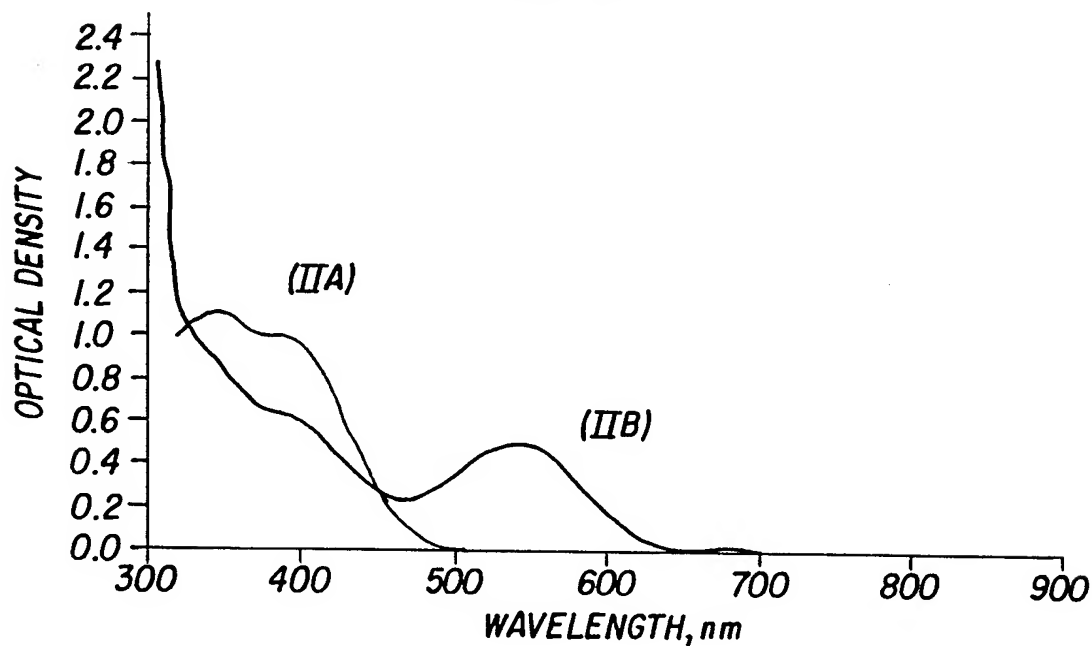
reading wavelengths, a thermal and time stability,

said photochromic compound has a high photochemical reversibility, thermal stability and has an absorption spectrum, which wavelength maximum coincides with the wavelength of frequency converted illumination, a thickness of said nonlinear compound and the value of nonlinearity of said nonlinear compound is in excess for the efficient frequency conversion, which method comprises:

a preparation of said photochromic compound and said nonlinear compound, and thereby  
converting of frequency by optical harmonic generation in said nonlinear compound,  
absorption of frequency converted illumination by said dye compound leading to fluorescence of said dye compound, and  
this fluorescent signal do not absorbs by neither said nonlinear compound and nor by said dye compound, and thereby  
possible two photon reading information from any layers of fluorescence multilayer ROM disk.



1/4

**FIG. 1****FIG. 2**

2/4

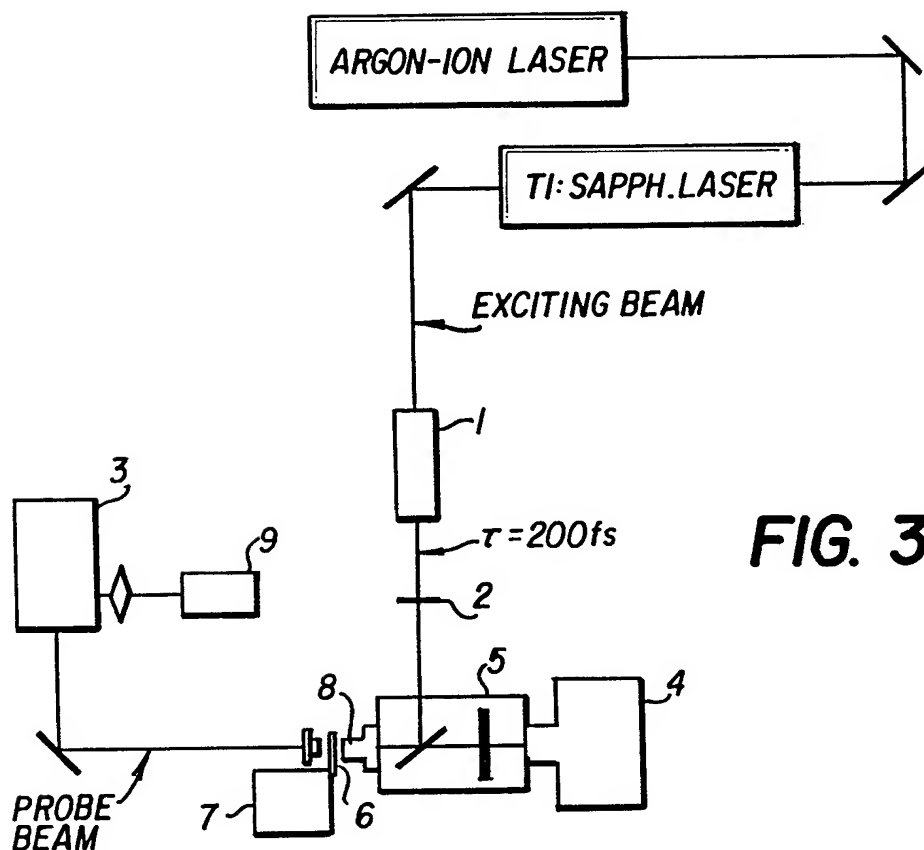
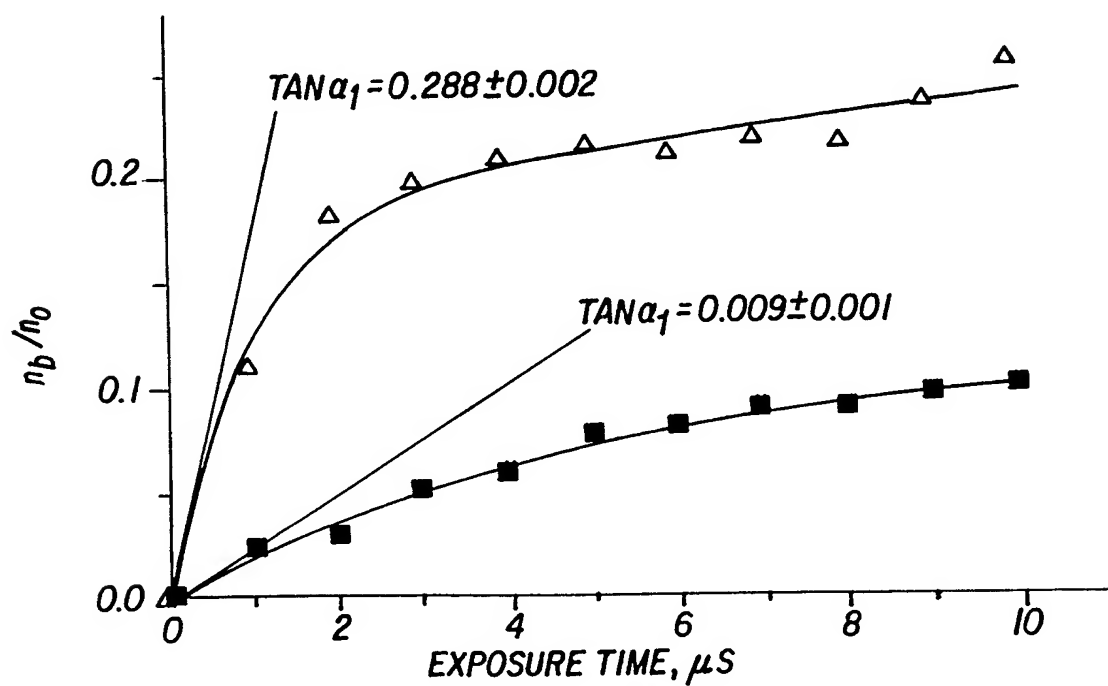
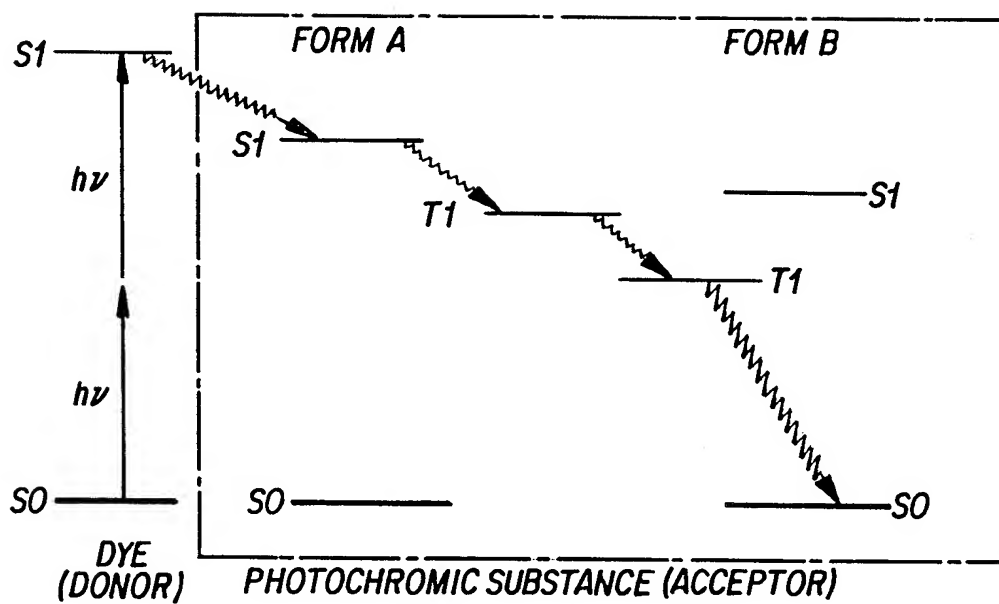
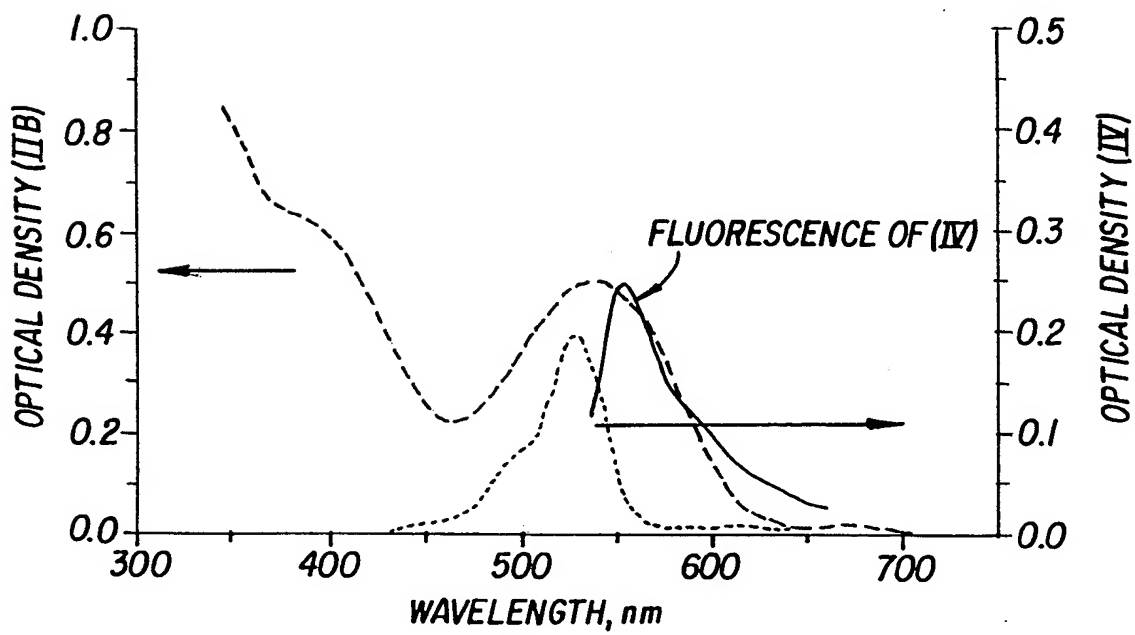


FIG. 3

FIG. 4



3/4

**FIG. 5****FIG. 6**

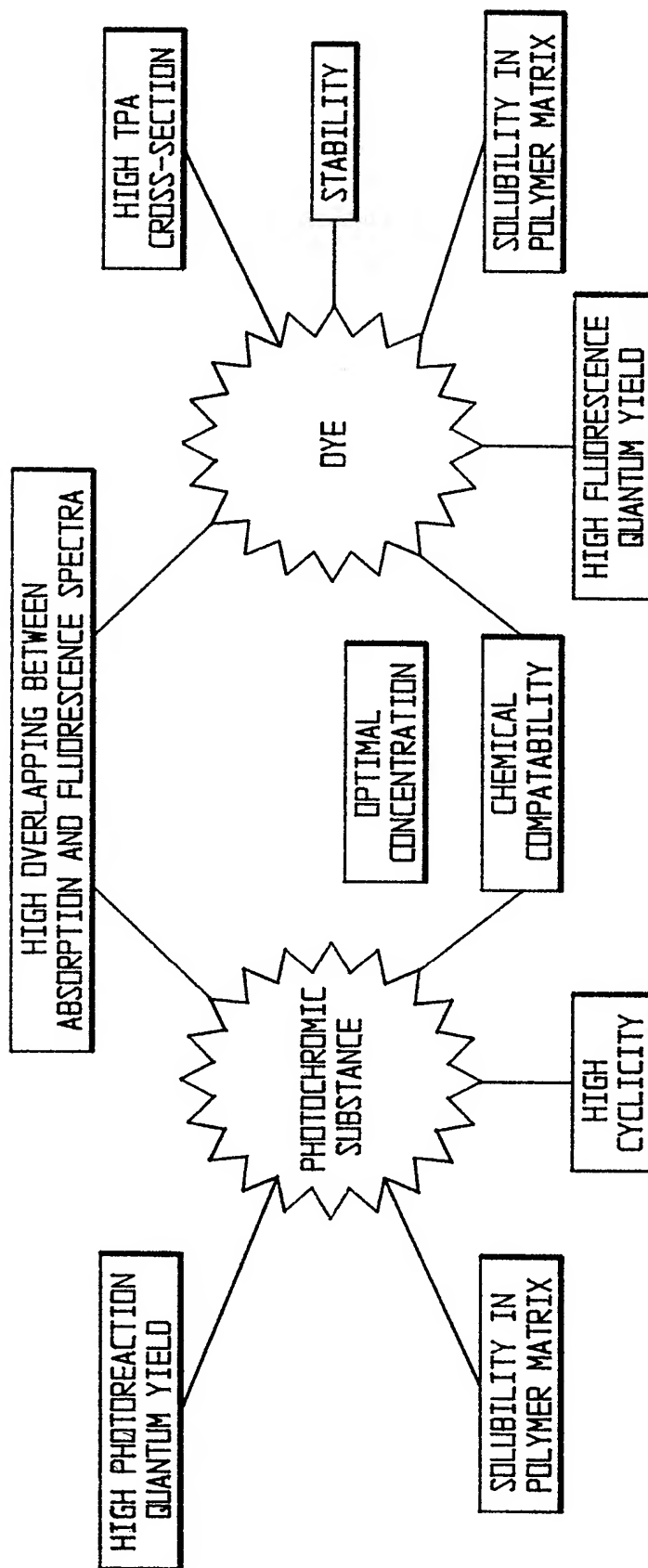


FIG. 7

## INTERNATIONAL SEARCH REPORT

 International application No.  
 PCT/US99/16419

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : G03C 1/73; G11B 7/24

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 430/19, 270.15, 273.1, 339, 345, 945; 365/111; 369/284, 288; 428/64.8

 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
 None

 Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
 STN, Search Terms : Photochromic and (nlo or nonlinear or non linear or fluoresce?)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ----- Y	KRIKUNOV, S.A., et al., "Efficiency enhance of writing information in 3D optical memory devices ..." INOCO '98 as disclosed in Proceed. SPIE, Vol 3733, pp. 326-333, held 6/3/98 through 7/3/98 in Moscow, Russia.	4-7 ----- 1-7
X	JP 03-284743 A (HASHIDA et al.) 16 December 1991, abstract.	1-3
X	JP 04-290794 A (FUKUCHI) 15 October 1992, abstract	4-7
X	JP 05-241268 A (HASHIDA et al.) 21 September 1993, abstract	1-3
X --- Y	JP 01-234489 A (SAIGA et al.) 19 September 1989, abstract	1-3 ----- 1-3



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E* earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*G* document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means	
*P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

04 OCTOBER 1999

Date of mailing of the international search report

04 NOV 1999

 Name and mailing address of the ISA/US  
 Commissioner of Patents and Trademarks  
 Box PCT  
 Washington, D.C. 20231  
 Facsimile No. (703) 305-3230

Authorized officer

MARTIN J. ANGEBRANDT

Telephone No. (703) 308-0661

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US99/16419

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	KOROTEEV, N.I., et al. "Reading 2.5D femptosecond optical data stroge system", Jap. J Appl. Phys. part 1, Volume 37 (4B), pp 2279-2280.	1-3 ---- 1-3

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US99/16419

## A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

430/19, 270.15, 273.1, 339, 345, 945; 365/111; 369/284, 288; 428/64.8